

Poly(2-acrylamido glycolic acid-co-2-acrylamido-2-methyl-1-propane sulfonic acid): Synthesis, Characterization, and Retention Properties for Environmentally Impacting Metal Ions

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ABSTRACT: Poly(2-acrylamido glycolic acid-co-2-acrylamido-2-methyl-1-propane sulfonic acid) [P(AGA-co-APSA)] was synthesized by radical polymerization in an aqueous solution. The water-soluble polymer, containing secondary amide, hydroxyl, carboxylic, and sulfonic acid groups, was investigated, in view of their metal-ion-binding properties, as a polychelator with the liquid-phase polymer-based retention technique under different experimental conditions. The investigated metal ions were Ag⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺, Pb²⁺, and Cr³⁺, and these were studied at pHs 3, 5, and 7. P(AGA-co-APSA) showed efficient retention of all metal ions at the pHs studied, with a mini-

mum of 60% for Co(II) at pH 3 and a maximum close to 100% at pH 7 for all metal ions. The maximum retention capacity (*n* metal ion/*n* polymer) ranged from 0.22 for Cd²⁺ to 0.34 for Ag⁺. The antibacterial activity of Ag⁺, Cu²⁺, Zn²⁺, and Cd²⁺ polymer-metal complexes was studied, and P(AGA-co-APSA)-Cd²⁺ presented selective antibacterial activity for *Staphylococcus aureus* with a minimum inhibitory concentration of 2 µg/mL. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 78–86, 2009

Key words: membranes; metal-polymer complexes; water-soluble polymers

INTRODUCTION

The metal-ion concentration needs to be reduced to acceptable levels in wastewater because metal ions are toxic and tend to bioaccumulate, and thus highly specific metal-ion-recovery processes are required. Several methods, such as ion exchange, adsorption, reverse osmosis, and precipitation, have been investigated to remove metal ions from polluted liquids.^{1,2}

Interactions between water-soluble polymers and metal ions take place in a homogeneous medium. Among the most promising techniques used to separate metal ions that are bound or not bound to polymers are membrane-process-based separation methods. Membrane filtration easily separates metal ions with the liquid-phase polymer-based retention (LPR) technique.^{3,4} Applications of water-soluble polymers to the homogeneous enrichment or selec-

tive separation of various metal ions from dilute solutions have been reported. Ultrafiltration is the most suitable technique for LPR studies.^{3–22,24,27} For use in homogeneous metal-ion recovery, the appropriate water-soluble polymers should present high water solubility, an easy, inexpensive synthesis route, an adequate molecular weight and molecular weight distribution, chemical stability, high affinity for one or more metal ions, and selectivity for the metal ion of interest.

The binding and elution processes can be formulated as a chemical reaction in which a reversible interaction reaction of the metal ion with the polymer in combination with an irreversible transfer of metal ions across the membrane is responsible for metal retention (see Scheme 1). Irreversible binding of metal ions to the polymer may also be found. The membrane's influence on the retention of metal ions inside the ultrafiltration cell is low and may be negligible in most cases.

Interactions of metal ions with water-soluble polymers are mainly due to electrostatic forces and to the formation of coordinating bonds. Other weak interactions may appear such as the entrapment of metal ions in the bulk of the polymer phase.

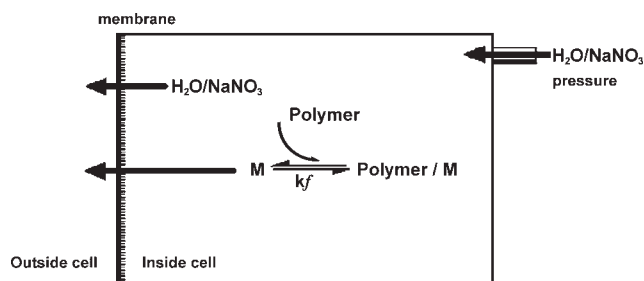
Water-soluble polymers with chelating groups are called polychelators. The coordination between polymers and metal ions may be described by the

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Scheme 1 General procedure of the LPR technique.

usual coordination theories, although certain special aspects should be considered. When intrachain complexes are predominant, the existence of a polymer domain with a nearly constant ligand concentration is normally recognized because the distances between them keep them in a narrow range for a given polymer chain. As a result, the chelating reaction appears as a one-step reaction. For relatively low ligand amounts in the solution, completely complexed metal ions may coexist with free, uncomplexed ones. Complex reactivity is sometimes strongly affected by the polymer ligand that exists outside the coordination sphere and surrounds the metal complex by means of special chemical, environmental, and steric effects.

The monomers 2-acrylamido-2-methyl-1-propane sulfonic acid (APSA) and 2-acrylamido glycolic acid (AGA) have been homopolymerized^{23–27} and copolymerized with several comonomers^{28,29} to form hydrogels³⁰ or suspensions³¹ that are able to respond to several stimuli^{32–34} and recover metal ions^{35–37} and whose biological effects as angiogenesis inhibitors³⁸ and anti-HIV prodrugs³⁹ have been studied.

The aim of this article is to report the synthesis of water-soluble polymers containing multiligand groups, to analyze their ability to remove environmentally impacting metal ions, and to study the bactericidal activity.

EXPERIMENTAL

Reagents

AGA (96%; molecular weight (MW) = 163.13 g/mol; Aldrich Co., St. Louis, MO) and APSA were used without further purification. Ammonium persulfate (Fluka) was used without further purification. Metal standard solutions of 1000 ppm were used:

Cr(NO₃)₃·9H₂O (98%, p.a.; Merck, Whitehouse Station, NJ), Co(NO₃)₂·6H₂O (99%, p.a.; Merck), Ni(NO₃)₂·6H₂O (99%, p.a.; Merck), Cu(NO₃)₂·3H₂O (99%, p.a.; Merck), Zn(NO₃)₂·6H₂O (extrapure; Merck), AgNO₃ (99.8%, p.a.; Merck), Cd(NO₃)₂·4H₂O (99%, p.a.; Merck), and Pb(NO₃)₂ (99%, p.a.; Merck). Sodium hydroxide (Merck) and 70% nitric acid (HNO₃; Caledon) were also used.

Polymer synthesis and purification

Poly(2-acrylamido glycolic acid-*co*-2-acrylamido-2-methyl-1-propane sulfonic acid) [P(AGA-*co*-APSA)] was obtained by radical polymerization of the monomers in an equimolar ratio. The monomers were added to the polymerization flask and dissolved to 100 mL with twice distilled water. Then, the initiator (ammonium persulfate) was added. The reaction was kept at 60°C for 24 h in an oil bath (see Table I). The polymer was purified and fractionated through ultrafiltration membranes with molecular mass cut-offs of 10,000, 30,000, and 100,000 Da. Fractions lower than 10,000 Da were discarded. Then, the polymers were lyophilized, polymer fractions were obtained with different molecular weights; these were characterized with Fourier transform infrared (FTIR) and ¹H-NMR spectroscopy. The polymerization yield was obtained from the sum of masses of fractions higher than 10,000 Da.

Polymer characterization

After polymer purification, the >100,000 Da fraction was characterized by FTIR and ¹H-NMR with deuterium oxide as the solvent and tetramethylsilane as the reference for 0.0 ppm.

P(AGA-*co*-APSA)

FTIR shows absorption signals corresponding to H–N at 3423 cm⁻¹, H–O at 3083 cm⁻¹, C–H at 2994 cm⁻¹, O=C–OH at 1739 cm⁻¹, O=C–N at 1655 cm⁻¹, C–N at 1455 cm⁻¹, ⁻O–C=O at 1396 cm⁻¹, S=O at 1343 cm⁻¹, C–O at 1220 cm⁻¹, C–OH at 1033 cm⁻¹, CH₂–COO^{-δ} at 805 cm⁻¹, and O–S–O at 621 cm⁻¹ (see Fig. 1).

The ¹H-NMR spectrum (250 MHz, D₂O, room temperature) shows the following absorption signals:

TABLE I
Amounts of the Monomers and Initiator Used for the Copolymerization Reaction

Polymer	AGA (mol)	APSA (mol)	AGA (g)	APSA (g)	Initiator ^a	
					(mol)	(g)
P(AGA- <i>co</i> -APSA)	0.03	0.03	4.89	6.21	0.0006	0.136

^a Ammonium persulfate.

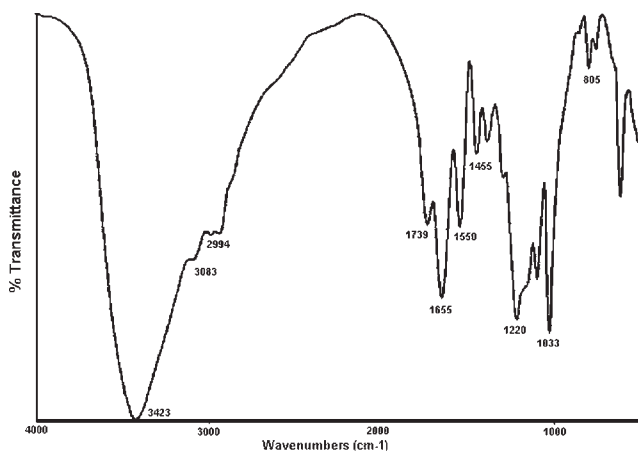


Figure 1 FTIR spectrum (KBr) of P(AGA-co-APSA).

C—CH₃ at 1.3–1.7 ppm, —CH₂— and —CH— at 1.9–2.6 ppm, —CH₂—S=O at 3.1–3.7 ppm, —NH—CH—OH at 5.2 ppm, and —OH, —COOH, and —SO₃H at 6.9–7.3 ppm (see Fig. 2). The copolymer composition was calculated with this technique using protons of —CH₂—S=O (area = 0.272) and —NH—CH—OH (area = 0.047) corresponding to APSA and AGA, respectively.

Light scattering measurements

To determine the polymer molecular weights and macromolecular dimensions, the polymers were studied as polyelectrolytes, being dissolved in twice distilled water, 0.5M HCl, NaCl, and Pb(NO₃)₂. Subsequently, 25 mL of the polymer solution was dialyzed for 72 h against 1 L of the electrolyte solution with constant stirring. All solutions were previously filtered with nylon filters of 0.22 μm for solutions and 0.45 μm for polymer dissolution.

Metal-ion retention by the LPR technique (the washing method)

To ensure a high level of ligand sites, the copolymer repeat unit/metal ion ratio (mol) was 40 : 1. A 20.0-mL solution containing 5.0×10^{-3} mequiv/L of a water-soluble copolymer (fraction > 100,000 Da) and 1.0×10^{-4} M metal ions was placed in the solution cell provided with an ultrafiltration membrane with a molecular mass cutoff of 10,000 Da (Millipore, Amicon, Billerica, MA). The metal ions studied at pHs 3, 5, and 7 were Ag⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺, Pb²⁺, and Cr³⁺.

The pH was adjusted with dilute HNO₃. A washing solution (water at pHs 3.0, 5.0, and 7.0, depending on the metal ion) was passed under pressure (3.5 bar of N₂) from the reservoir through the cell solution. As the influx and outflux were rapidly equaled, the initial volume (20.0 mL) was kept con-

stant during the experiment. Ten fractions of 20 mL were collected. Each fraction was collected in graduated tubes, and the corresponding metal-ion concentration was determined by atomic absorption spectroscopy.

Determination of the maximum retention capacity (MRC) by the LPR technique (the concentration method)

To obtain polymer–metal complexes, the LPR technique by the concentration method was used. The metal ions studied were selected for their known antibacterial activity and low toxicity level: Ag⁺, Cu²⁺, Zn²⁺, and Cd²⁺.

This method consists of passing a metal-ion solution with a known concentration through a solution of a water-soluble polymer (20 mL) while a constant volume is maintained. The enrichment (or concentration) method requires that the water-soluble polymer be placed in the ultrafiltration cell and that the metal-ion solution be placed in the reservoir. When metal ions pass through the ultrafiltration cell, the macromolecules uptake the metal ions until saturation, and the nonretained metal ions are collected in 5- and 10-mL assay tubes and quantified by atomic absorption spectroscopy. Because these polymer–metal complexes were going to be used to determine antibacterial activity, an elution with 100 mL of twice distilled water was made after each MRC experiment to eliminate all the metal ions not bounded to the polymer to observe only the polymer–metal complex effect. The same >100,000 Da fraction and 10,000 Da membranes were employed in this study. A blank experiment with metal ions and without the polymer was required to determine the effect of the ultrafiltration membrane on metal retention. The amount of metal ion bound to the water-soluble polymer was calculated from the difference between the concentration curves' slopes and the blank curves.

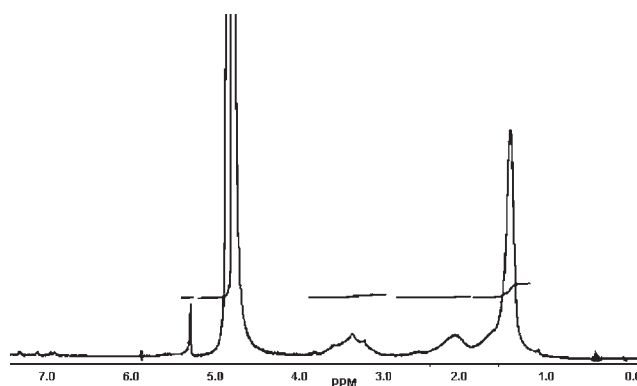
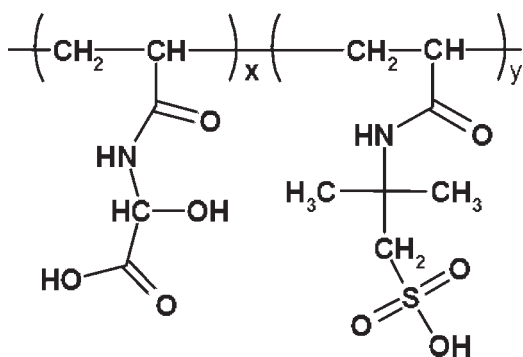


Figure 2 ¹H-NMR spectrum (250 MHz, D₂O, room temperature) of P(AGA-co-APSA).



Scheme 2 General structure of the water-soluble interaction.

MRC was calculated with the following relationship:

$$\text{MRC} = MV/P_m$$

where MRC is expressed as milligrams of the metal ion retained per gram of the polymer (or as moles), M is the metal-ion concentration (mg/L), V is the filtrate volume passing through the membrane free of metal ion (L), and P_m is the mass of the polymer (g).

Antibacterial activity of the polymer and polymer-metal complexes

The antibacterial activity of the polymer, polymer-metal complexes, and free metal ions was investigated for *Escherichia coli* (6538P), a gram-negative bacterium, and *Staphylococcus aureus* (ATCC 28922), a gram-positive bacterium. Antibacterial activity was evaluated with the National Committee for Clinical Laboratory Standards method. According to that method, different aqueous solutions of the compounds were prepared. The concentrations of these solutions were 1, 2, 4, 8, 16, 32, 64, 128, 256, 512, 1024, and 2040 g/mL. These solutions were inoculated with those corresponding bacteria and then incubated for 24 h at 37°C with a nutrient solution of soy trypticase. This experiment was used to determine the minimum inhibitory concentration (MIC), that is, the

minimum concentration of a compound stopping the growth without necessarily killing the bacteria.

Measurements

The FTIR spectra were recorded on a Magna Nicolet (Billerica, MA) 550 spectrophotometer. $^1\text{H-NMR}$ spectra were recorded on a Bruker (Ettingen, Germany) AC 250 spectrometer. The pH was determined with a Jenco Electronics 1671 pH-meter. For the LPR technique, a membrane filtration system was employed to test the coordinating properties of the polychelator. A Unicam Solaar (Cambridge, UK) M5 series atomic absorption spectrometer was used for the determination of the metal-ion concentrations in the filtrate. Molecular weights were determined by light scattering in a Wyatt Dawn DSP-F photometer and a Wyatt Optilab 903 interferometric refractometer (Wyatt Technology Co., Santa Barbara, CA). Bacterial growth was determined by direct observation and comparison with a blank sample.

RESULTS AND DISCUSSION

P(AGA-co-APSA), obtained by radical polymerization, is soluble in water with a 97% yield. According to the yield, this polymer could have a copolymer composition very close to 1 : 1 with a random distribution on the polymer chain due to radical polymerization. The $^1\text{H-NMR}$ spectrum for the >100,000 Da fraction showed isolated signals for $\text{CH}_2\text{-SO}_3\text{H}$ protons and NH-CH-OH proton, with the areas indicated in the Experimental section; this gave a comonomer ratio of 0.33 : 1.00 (AGA/APSA). The chemical structure of this random copolymer is shown in Scheme 2, where $x = 0.33$ and $y = 1.00$.

The molecular weight of P(AGA-co-APSA) was determined by light scattering. It showed a diminished mean square root due to the addition of twice distilled water and 0.5M HCl. An addition of 0.5M NaCl or $\text{Pb}(\text{NO}_3)_2$ at this concentration resulted in an insoluble polymer (see Fig. 3 and Table II); different observations were made in the LPR experiments because a lower concentration was required to

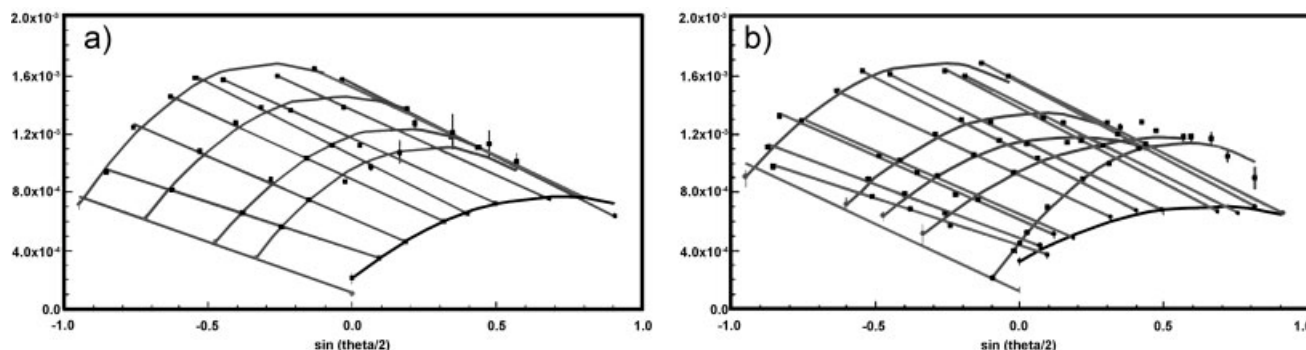


Figure 3 Zimm plots for (a) P(AGA-co-APSA) in twice distilled water and (b) P(AGA-co-APSA) in 0.5M HCl.

TABLE II
Macromolecular Parameters of P(AGA-co-APSA)

Sample	Solution	Molecular weight (g/mol)	Root mean square
P(AGA-co-APSA)	Twice distilled water	$3.28 \pm 0.8e7$	116.8 ± 7.5
	0.5M HCl	$2.90 \pm 0.3e6$	56.4 ± 15.1
	0.5M NaCl	—	—
	Pb(NO ₃) ₂	—	—

perform the experiment, and a soluble polymer was obtained.

Effect of the pH on metal-ion retention

The water-soluble polymer P(AGA-co-APSA) shows four possible ligand sites in its structure: carboxylic

acid, sulfonic acid, amide, and hydroxyl groups. The washing method was used to evaluate the polymer-metal-ion retention capability. The retention profile results are shown in Figure 4.

Different acidic compositions are present in this polymer's structure: a weak polyelectrolyte (e.g., carboxylic acid from AGA with $pK_a = 4.37$) and a strong polyelectrolyte (e.g., sulfonic acid from APSA with $pK_a = 1$). The interaction with the eight metal ions is high at all pHs. At pH 3, sulfonic acid is completely deprotonated and carboxylic acid is protonated; at pH 5, the carboxylic acid groups are partially deprotonated; and at pH 7, all the groups are deprotonated.

A summary of the interactions at $Z = 10$ is presented in Figure 5 for all pHs. At pH 3, the interaction with all metal ions is high, basically because of the presence of the sulfonate group, with values

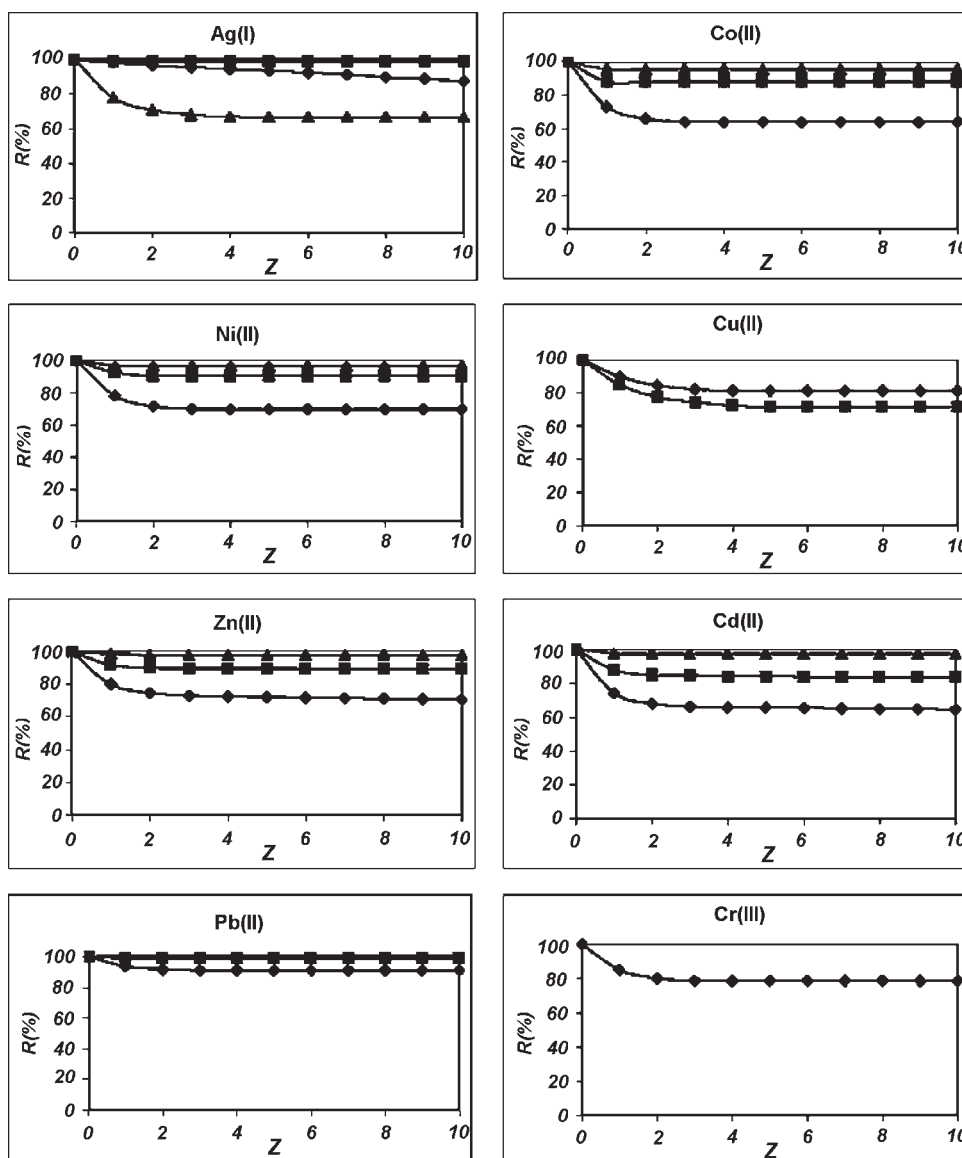


Figure 4 Retention profile of P(AGA-co-APSA) at different pHs [amount of copolymer = 0.042 mg; copolymer/metal ion ratio (mmol of repeat unit/metal) = 40 : 1].

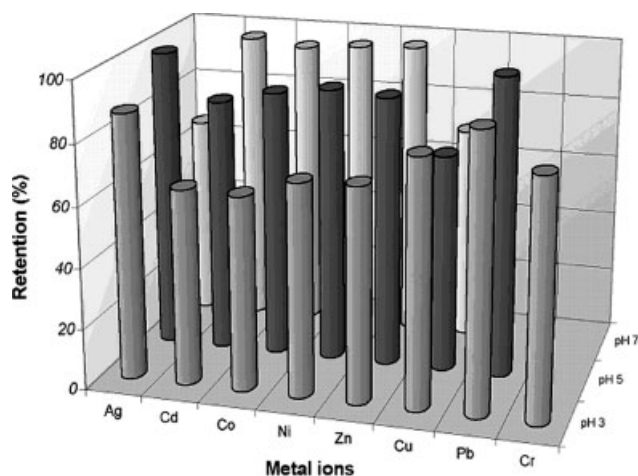


Figure 5 MRC of P(AGA-co-APSA) ($Z = 10$) for all metal ions at pHs 3, 5, and 7.

ranging from 63% for Co^{2+} to 90% for Pb^{2+} . When the pH increases to pH 5, the carboxylic acid groups are partially deprotonated, and the interaction is higher, rising to 90% for all metal ions, except for Cu^{2+} , for which it remains close to 70%. Because of the precipitation of hydroxyl species at pH 5, Cr^{3+} could not be studied. The increased interaction indicates that the copolymer has higher efficiency or cooperation between monomers. The comparison with the Ag^+ retention pattern for water-soluble homopolymers confirms the explanation because 35% retention for poly(2-acrylamido glycolic acid)²⁷ and 50% retention for poly(2-acrylamido-2-methyl-1-propane sulfonic acid)²⁴ can be found, whereas the copolymer P(AGA-co-APSA) reaches a maximum of 98% retention at this pH. Finally, at pH 7, when the copolymer is completely deprotonated, the retention is highest for all divalent metal ions (Co^{2+} , Ni^{2+} , Zn^{2+} , and Cd^{2+}), with values close to 100%, except for Cu^{2+} , for which it remains constant at 70%. Retention decreases only for Ag^+ , and this may be due to displacement for the interaction with divalent metal ions, although it is higher than that of poly(2-acrylamido-2-methyl-1-propane sulfonic acid) at all pHs. The study of Cu^{2+} at pH 7 [without precipitation of $\text{Cu}(\text{OH})_x$] is possibly due to the low concentration used, although Cr^{3+} and Pb^{2+} precipitated at this pH by forming hydroxyl species. In Figure 4, the retention stability can be observed to be achieved at $Z = 4$ for all pHs investigated, and this indicates a fast equilibrium and a strong interaction between the metal ion and polymer in a water solution.

The different ligand sites involved and the effect of the polychelator microstructure also influence this behavior. In principle, the ligand sites come from the AGA and APSA moieties for both copolymers. However, the differences in the retention pattern indicate that the amide groups are involved in

the polymer-metal-ion interaction and/or there is a synergic effect.

If we consider Pearson's HSAB principle,⁴⁰ the polymer behavior can be explained as a polychelator. The AGA moiety has hydroxyl, amide, and carboxylic groups, and all groups are classified as soft bases; APSA has amide and sulfonic groups, and they are soft and hard bases, respectively. According to the HSAB principle, the ligands of P(AGA-co-APSA) can interact with metal ions classified as hard (Cr^{3+}) and borderline (Ni^{2+} , Co^{2+} , Cu^{2+} , Zn^{2+} , and Pb^{2+}) acids at pHs 3, 5, and 7, and they can interact with soft (Ag^+ and Cd^{2+}) acids at pHs 5 and 7. The results are in agreement with the retention results, in which an interaction was observed with all metal ions at all pHs, and the behavior is similar for all ions belonging to a single classification.

On the basis of the metal-ion retention results and the antibacterial study, Cu^{2+} -polymer, Zn^{2+} -polymer, Cd^{2+} -polymer, and Ag^+ -polymer complexes were prepared. pH 7 was selected for all metal ions except for the Cu^{2+} complex, which was at pH 5 (to avoid the formation of hydroxyl species at this concentration). All the complexes obtained were water-soluble. The Ag^+ complex was highly photosensitive and was quickly oxidized to Ag^0 . MRC (n metal ion/ n polymer) changed from 0.22 for Cd^{2+} to 0.34 for Ag^+ . Details are presented in Table III and Figure 6. After that, these complexes were washed with twice distilled water to eliminate the free metal ion in equilibrium in solution. Electron microscopy images of the dry polymer and its complexes are presented in Figure 7. It is possible to observe a great difference between surfaces, from no porosity to high porosity for the P(AGA-co-APSA)- Cd^{2+} complex, but this increase in porosity is not indicative of an increase in solubility.

Polymer-metal-ion interaction mechanism

On the basis of absorption signals from FTIR spectra of the P(AGA-co-APSA) homopolymers and their polymer-metal complexes with Cu^{2+} and Cd^{2+} as well as the functional groups of the polymer structure, two kinds of polymer-metal-ion interactions

TABLE III
MRC of P(AGA-co-APSA) for Cu^{2+} at pH 5 and for Zn^{2+} , Cd^{2+} , and Ag^+ at pH 7

Metal ion	MRC of P(AGA-co-APSA)	
	n metal/ n polymer	mg of metal/g of polymer
Cu^{2+}	0.30	103.0
Zn^{2+}	0.28	99.2
Cd^{2+}	0.22	39.7
Ag^+	0.34	198.9

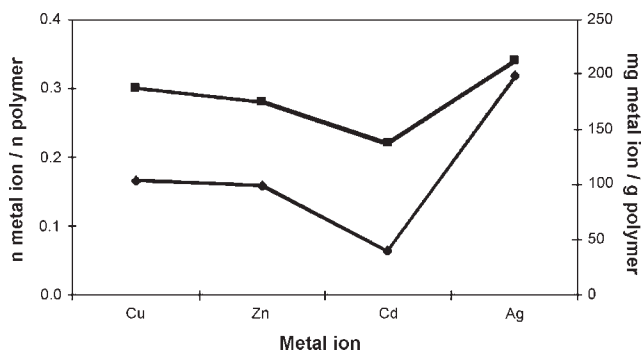


Figure 6 MRC of P(AGA-co-APSA) for Cu^{2+} at pH 5 and for Zn^{2+} , Cd^{2+} , and Ag^+ at pH 7.

can be obtained. These involve interactions with carboxylate ($-\text{COO}^-$) and amide [$(\text{C}=\text{O})\text{N}-$] groups, by themselves or in a combination of both groups forming a complexation mechanism. Throughout the interactions, sulfonate ($-\text{SO}_3^-$) groups can be formed by an electrostatic mechanism. In Figure 8(a), shifts can be observed in the FTIR spectra for these materials; all of them have the same signals, although the signal of $\text{HO}-\text{C}=\text{O}$, from AGA at 1739 cm^{-1} , disappears for both complexes, moving to the same wave number of $-\text{NH}-\text{C}=\text{O}$ and appearing as $^-\text{O}-\text{C}=\text{O}_{\text{asr}}$, which indicates a coordination-type interaction. The $^-\text{O}-\text{C}=\text{O}_{\text{vs}}-\text{M}$ interaction is less sensitive than $^-\text{O}-\text{C}=\text{O}_{\text{asr}}$, and its signals do not have important changes. The $\text{C}-\text{O}$ stretching band

of $\text{C}-\text{OH}$ presents a shift from 1031 to 1034 and 1039 cm^{-1} for the Cu^{2+} complex and Cd^{2+} complex, respectively. APSA as a strong acid produces only long-range interactions, whereas the $\text{O}-\text{S}-\text{O}$ frequency at 621 cm^{-1} does not present significant differences. Far FTIR spectra are shown in Figure 8(b), where it is possible to observe significant differences at low frequencies from 292 to 307 cm^{-1} for the Cu^{2+} complex and 319 cm^{-1} for the Cd^{2+} complex, which can be attributed to N -metal interactions (see Scheme 3).

Antibacterial activity

With the polymer-metal-ion complexes synthesized, the minimum bactericidal concentration was investigated for P(AGA-co-APSA), its complexes, and free metal ions. Results are summarized in Table IV. Ag^+ , Cu^{2+} , and Zn^{2+} complexes present low antibacterial activity in comparison with free metal ions and other polymer-metal complexes. Cd^{2+} , a heavy metal with well-known high toxicity, has good and very specific antibacterial activity against *S. aureus*. Other complexes present behavior similar to that of free metal ions, as expected because of the presence of a structural difference in the cell wall of gram-positive bacteria that is not present in gram-negative bacteria (*E. coli*). The low antibacterial activity of the Ag^+ complex can be explained by the complex's low

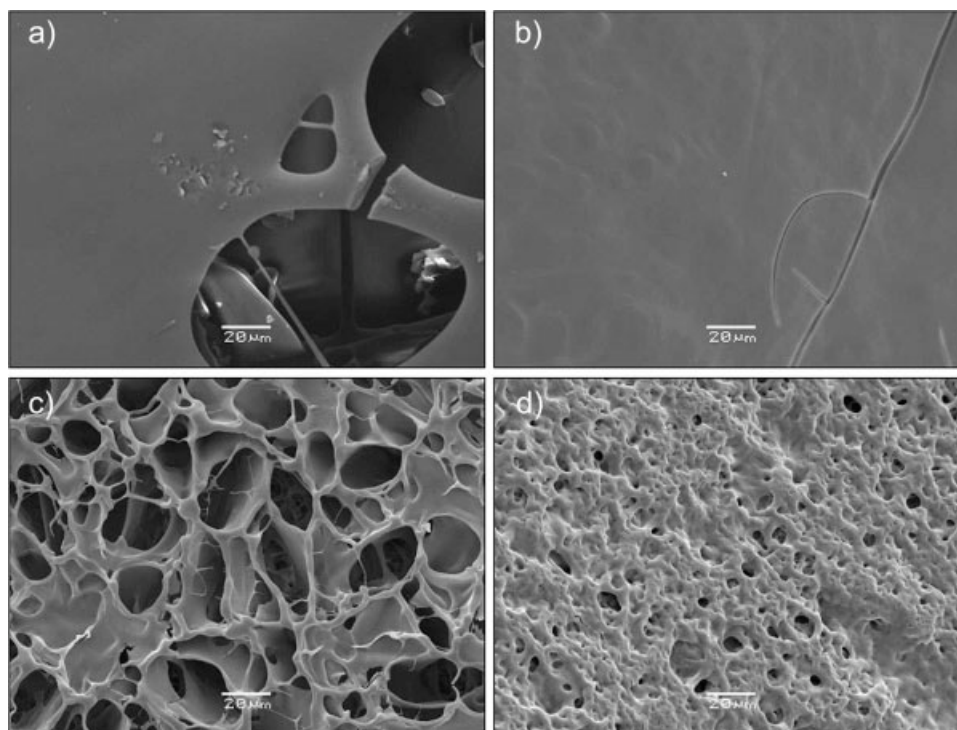


Figure 7 Scanning electron micrographs for (a) P(AGA-co-APSA), (b) P(AGA-co-APSA)- Cu^{2+} , (c) P(AGA-co-APSA)- Zn^{2+} , and (d) P(AGA-co-APSA)- Cd^{2+} .

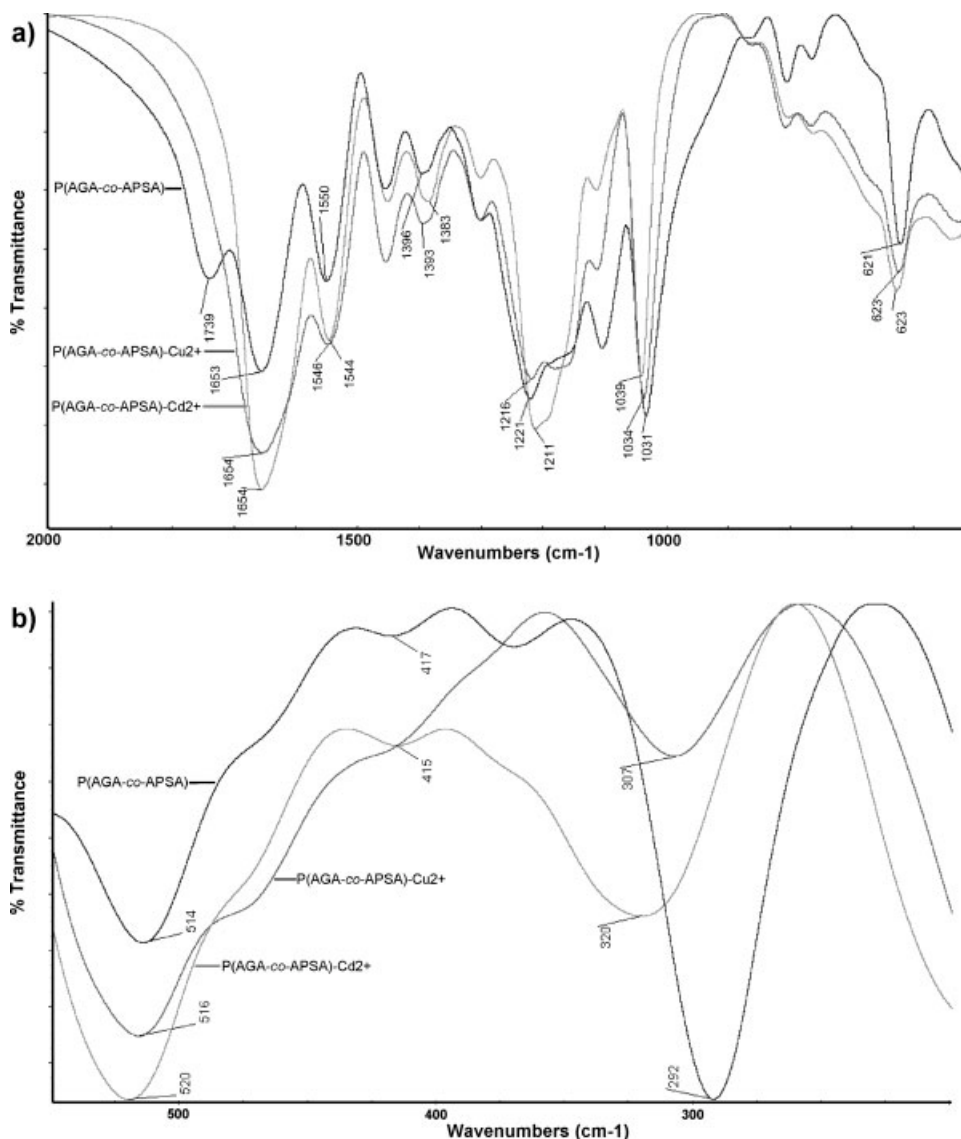
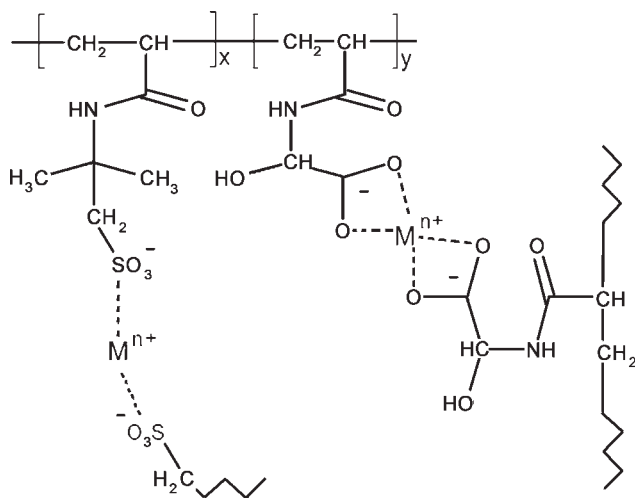


Figure 8 (a) FTIR spectra of P(AGA-co-APSA) (black line), P(AGA-co-APSA)-Cu²⁺ (gray line), and P(AGA-co-APSA)-Cd²⁺ (light gray line) and (b) far FTIR spectra of P(AGA-co-APSA), P(AGA-co-APSA)-Cu²⁺, and P(AGA-co-APSA)-Cd²⁺.



Scheme 3 Suggested polymer-metal ion interaction.

TABLE IV
MIC Values for P(AGA-co-APSA), Its Complexes, and Free Metal Ions Against *E. coli* (ATCC 28922) and *S. aureus* (6359P)

Sample	MIC (µg/mL)		Metal concentration (µg/mL)	
	<i>E. coli</i>	<i>S. aureus</i>	<i>E. coli</i>	<i>S. aureus</i>
Ag ⁺	16	16	—	—
Cu ²⁺	2040	256	—	—
Zn ²⁺	>2040	128	—	—
Cd ²⁺	2040	2	—	—
P(AGA-co-APSA)	>2040	>2040	—	—
P(AGA-co-APSA)-Ag ⁺	2040	1024	0.4	0.2
P(AGA-co-APSA)-Cu ²⁺	>2040	1024	>0.2	0.1
P(AGA-co-APSA)-Zn ²⁺	>2040	512	>0.2	0.05
P(AGA-co-APSA)-Cd ²⁺	> 2040	4	>0.08	0.00016

stability, which reduces the Ag^+ concentration in the polymer over time.

CONCLUSIONS

A novel water-soluble polymer, P(AGA-co-APSA), was synthesized by radical polymerization. This water-soluble polymer, containing amide, hydroxyl, carboxylic, and sulfonic acid groups, was studied as a polychelator with the LPR technique. P(AGA-co-APSA) was found to effectively retain all metal ions studied at all pHs with a fast, strong interaction. Its metal-ion complexes showed a high molar metal-ion/polymer interaction relationship involving sulfonic groups by electrostatic interactions and carboxylic and possibly amide groups from both monomers by mean complex formation, increasing the Ag^+ retention in comparison with its homopolymer. The copolymer's activity as an antibacterial reagent was low, whereas the polymer-metal-ion complex had higher activity for gram-positive bacteria. Only P(AGA-co-APSA)- Cd^{2+} presented efficient antibacterial activity against *S. aureus* with an MIC value of 4 $\mu\text{g}/\text{mL}$.

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